a product in which two R-DAB's are linked, $[Ru_2(CO)_5(R\text{-}IAE)$ (3)], and a cluster product $[Ru_4(CO)_8(R\text{-}DAB)_2$ (4)], respectively. The reaction with R-DAB, yielding $Ru_2(CO)_5(R\text{-}IAE)$, proves that $Ru_2(CO)_5(R\text{-}DAB)$ is an intermediate in the earlier developed reaction of $Ru_2(CO)_6(R\text{-}DAB)$ with R-DAB.

Supplementary Material Available: Listings of elemental analyses data, anisotropic thermal parameters, bond lengths and bond angles, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Preparation, Crystal Structure, and Spectroscopic Characterization of $[NEt_4]_2[Cu(SPh)_3]$

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Received August 9, 1983

A new and convenient synthesis of $[Cu(SPh)_3]^{2-}$ involves the treatment of $[(Ph_3PCuCl)_4]$ with $[NEt_4]SPh$ (1:20) in MeCN. $[NEt_4]_2[Cu(SPh)_3]$ crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.116$ (2) Å, $b = 13.107$ (2) Å, $c = 30.677$ (4) Å, $\beta = 95.39$ (1)°, $V = 3649$ Å^3, and $Z = 4$. The structure was solved by conventional Patterson and Fourier syntheses, and 4075 unique reflections were used in the refinement, which converged at $R = 0.074$. The copper(I) atom is coordinated by a trigonal-planar array of three sulfur atoms ($\overline{\text{Cu–S}} = 2.250$ (9) Å). IR, Raman, UV/visible, and ^{1}H NMR spectra are presented for this compound.

The preparation and crystal structure of $[PPh_4]_2[Cu(SPh)_3]$ have been reported by Coucouvanis et al.[2] This complex anion is of interest because, at present, it is the simplest fully characterized copper–thiolate complex and is thus valuable for the definition and interpretation of the spectroscopic properites typical of copper(I)–thiolate interactions. We were interested in this system, together with other copper(I)–thiolate clusters, particularly those prepared by Coucouvanis et al.[2,3] and Dance,[3] as possible models of the copper–cysteinyl aggregates suggested for metallothioneins, especially to aid interpretation of EXAFS data[4] for these proteins.

Investigations of the reactions of copper complexes with benzenethiolate have led to the following observations: (i) $[Cu(SPh)_3]^{2-}$ may be readily prepared in good yield by treating $[(Ph_3PCuCl)_4]$[5] with $[NEt_4]SPh$ (1:20), (ii) $[Cu(SPh)_3]^{2-}$ is intrinsically colorless *not* orange-red as previously observed in the $[PPh_4]^+$ salt,[2] and (iii) the Cu–S bond lengths for this anion, with $[NEt_4]^+$ as the cation, are more regular and, on average, slightly shorter than those reported[2] for the $[PPh_4]^+$ salt. These results, together with IR, Raman, UV/visible, and ^{1}H NMR spectra for $[NEt_4]_2[Cu(SPh)_3]$, are detailed herein.

Experimental Section

All manipulations were accomplished under an atmosphere of purified dinitrogen and the solvents used were purged with this gas. $[NEt_4]Cl$ (Fluka, 1.14 g, 6.88 mmol), dried by heating at ca. 100 °C in vacuo for ca. 4 h, was suspended in dry MeCN (normal commercial grade, ca. 7 cm^3). KSPh (1.02 g, 6.88 mmol) was added and the mixture stirred at room temperature for ca. 4 h. The precipitate thus obtained was removed by filtration, and to the resultant solution of $[NEt_4]SPh$ was added $[(Ph_3PCuCl)_4]$[5] (0.5 g, 0.34 mmol). The mixture was stirred at room temperature, and a clear solution was obtained after ca. 10 min, which was subsequently evaporated to dryness, under a reduced pressure and without heating. The off-white solid so obtained was washed three times with toluene (10-cm^3 portions) to remove Ph_3P and dried in vacuo. This solid was extracted into refluxing i-Pr_2O/MeCN (3 cm^3; 50:50 mixture by volume). Colorless needle-shaped crystals were obtained from this pale green/yellow solution upon slow cooling. These crystals were isolated by filtration, washed twice with a cold recrystallization medium, (ca. 2.0-cm^3 portions), and dried in vacuo; typical yield ca. 0.62 g (70%).

Anal. Calcd for $C_{34}H_{55}N_2CuS_3$: C, 62.7; H, 8.5; N, 4.3; Cu, 9.8; S, 14.8. Found: C, 62.5; H, 9.0; N, 4.5; Cu, 9.6; S, 14.4.

IR spectra were recorded on Perkin-Elmer 577 and 225 spectrometers, and Raman data were collected by using 514.5-nm excitation on a Spex double-monochromator Raman spectrometer. UV/visible absorptions were monitored ona Perkin-Elmer 402 spectrometer and the ^{1}H nuclear magnetic resonances observed at 300 MHz on a Varian SC-300 instrument.

Crystal Structure Determination

Crystals prepared as described above proved suitable for X-ray crystallographic studies. Measurements were made at room temperature on a Stoe-Siemens AED four-circle diffractometer, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), from a crystal of dimensions 0.7 × 0.5 × 0.3 mm (parallelpiped with edges parallel to unit cell axes) sealed in a capillary tube. Cell dimensions were calculated by least-squares methods from the 2θ values ($20 < 2\theta < 25°$) of 52 centered reflections. The space group is $P2_1/c$ with $a = 9.116(2)$ Å, $b = 13.107$ (2) Å, $c = 30.677$ (4) Å, $\beta = 95.39$ (1)°, $V = 3649$ Å^3, $Z = 4$, and $D_{calcd} = 1.19$ g cm^{-3}.

Intensities were measured by a real-time profile-fitting method,[6] in a θ/ω scan mode for a unique set of reflections with $2\theta < 50°$; h, $k \geq 0$. Numerical absorption corrections were applied ($\mu = 7.87$ cm^{-1}, transmission 0.62–0.72). Of the 6390 unique data, 4075 with $F > 4\sigma(F)$ were used for the structure determination.[7] There was no significant variation in the intensities of three check reflections monitored regularly during the data collection.

The copper atom was located in a Patterson synthesis, and other atoms were located in subsequent difference maps. Hydrogen atoms were constrained [C–H = 0.96 Å, methyl H–C–H = 109.5°, aromatic H on C–C–C external bisector; $U(H) = 1.2U_{eq}(C)$, where $U_{eq}(C)$ is the equivalent isotropic thermal parameter for a C atom[8]]; all other atoms were refined with anisotropic thermal parameters, by a blocked

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Table I. Atomic Coordinates ($\times 10^4$)[a] of $[NEt_4]_2[Cu(SPh)_3]$

atom	*x*	*y*	*z*
Cu	7351 (1)	5647 (1)	1494 (1)
S(1)	7576 (2)	3968 (1)	1641 (1)
C(11)	8020 (6)	3235 (4)	1195 (2)
C(12)	8387 (7)	2207 (4)	1266 (2)
C(13)	8661 (8)	1593 (5)	914 (2)
C(14)	8596 (8)	1946 (5)	498 (3)
C(15)	8238 (7)	2968 (6)	423 (2)
C(16)	7969 (6)	3600 (5)	773 (2)
S(2)	8581 (2)	6294 (1)	951 (1)
C(21)	7958 (7)	7496 (5)	757 (2)
C(22)	8742 (7)	8013 (5)	453 (2)
C(23)	8257 (10)	8918 (6)	278 (2)
C(24)	7001 (11)	9367 (6)	402 (3)
C(25)	6239 (9)	8889 (5)	711 (3)
C(26)	6718 (7)	7977 (5)	890 (2)
S(3)	6064 (2)	6677 (1)	1899 (1)
C(31)	5364 (5)	6091 (4)	2353 (2)
C(32)	5043 (6)	6693 (5)	2710 (2)
C(33)	4424 (7)	6288 (6)	3062 (2)
C(34)	4103 (7)	5253 (5)	3079 (2)
C(35)	4425 (6)	4653 (5)	2734 (2)
C(36)	5035 (6)	5055 (4)	2369 (2)
N(4)	8986 (5)	3453 (4)	3085 (2)
C(41)	8380 (7)	4434 (5)	2885 (2)
C(42)	9192 (12)	5412 (6)	3055 (3)
C(43)	8953 (7)	3440 (6)	3583 (2)
C(44)	7411 (9)	3615 (7)	3736 (3)
C(45)	8028 (7)	2617 (5)	2867 (2)
C(46)	8522 (8)	1567 (6)	2987 (3)
C(47)	10589 (6)	3292 (5)	3006 (2)
C(48)	10856 (8)	3281 (7)	2536 (3)
N(5)	3081 (5)	3900 (4)	822 (2)
C(51)	4043 (10)	2976 (7)	965 (4)
C(52)	3285 (12)	1923 (7)	893 (4)
C(53)	1669 (8)	3900 (8)	1023 (3)
C(54)	1893 (11)	3858 (10)	1535 (3)
C(55)	4033 (9)	4802 (6)	961 (3)
C(56)	3413 (11)	5809 (7)	818 (3)
C(57)	2685 (10)	3876 (8)	331 (3)
C(58)	4160 (12)	3674 (10)	99 (3)

[a] Estimated standard deviations in the last place of figures are given in parentheses in all tables.

Table II. Bond Lengths (Å) and Angles (deg) for $[NEt_4]_2[Cu(SPh)_3]$

Cu-S(1)	2.253 (2)	Cu-S(2)	2.258 (2)
Cu-S(3)	2.239 (2)	S(1)-C(11)	1.750 (6)
C(11)-C(12)	1.401 (8)	C(11)-C(16)	1.379 (8)
C(12)-C(13)	1.389 (10)	C(13)-C(14)	1.352 (10)
C(14)-C(15)	1.392 (10)	C(15)-C(16)	1.396 (9)
S(2)-C(21)	1.760 (6)	C(21)-C(22)	1.402 (9)
C(21)-C(26)	1.389 (9)	C(22)-C(23)	1.359 (10)
C(23)-C(24)	1.372 (13)	C(24)-C(25)	1.378 (12)
C(25)-C(26)	1.369 (9)	S(3)-C(31)	1.763 (6)
C(31)-C(32)	1.401 (8)	C(31)-C(36)	1.393 (8)
C(32)-C(33)	1.371 (9)	C(33)-C(34)	1.390 (10)
C(34)-C(35)	1.372 (9)	C(35)-C(36)	1.398 (9)
N(4)-C(41)	1.506 (8)	N(4)-C(43)	1.531 (8)
N(4)-C(45)	1.517 (8)	N(4)-C(47)	1.519 (7)
C(41)-C(42)	1.546 (11)	C(43)-C(44)	1.541 (11)
C(45)-C(46)	1.484 (10)	C(47)-C(48)	1.485 (10)
N(5)-C(51)	1.535 (11)	N(5)-C(53)	1.478 (9)
N(5)-C(55)	1.503 (10)	N(5)-C(57)	1.516 (9)
C(51)-C(52)	1.550 (13)	C(53)-C(54)	1.566 (12)
C(55)-C(56)	1.487 (12)	C(57)-C(58)	1.602 (14)

S(1)-Cu-S(2)	118.2 (1)	S(1)-Cu-S(3)	121.3 (1)
S(2)-Cu-S(3)	120.3 (1)	Cu-S(1)-C(11)	113.7 (2)
S(1)-C(11)-C(12)	118.4 (4)	S(1)-C(11)-C(16)	123.7 (5)
C(12)-C(11)-C(16)	117.8 (5)	C(11)-C(12)-C(13)	119.5 (6)
C(12)-C(13)-C(14)	122.7 (6)	C(13)-C(14)-C(15)	118.4 (7)
C(14)-C(15)-C(16)	119.9 (6)	C(11)-C(16)-C(15)	121.6 (6)
Cu-S(2)-C(21)	114.8 (2)	S(2)-C(21)-C(22)	119.3 (5)
S(2)-C(21)-C(26)	123.6 (5)	C(22)-C(21)-C(26)	117.1 (6)
C(21)-C(22)-C(23)	121.1 (7)	C(22)-C(23)-C(24)	120.9 (8)
C(23)-C(24)-C(25)	118.9 (7)	C(24)-C(25)-C(26)	120.7 (7)
C(21)-C(26)-C(25)	121.1 (6)	Cu-S(3)-C(31)	115.1 (2)
S(3)-C(31)-C(32)	119.3 (4)	S(3)-C(31)-C(36)	123.2 (4)
C(32)-C(31)-C(36)	117.4 (5)	C(31)-C(32)-C(33)	121.9 (6)
C(32)-C(33)-C(34)	120.7 (6)	C(33)-C(34)-C(35)	118.0 (6)
C(34)-C(35)-C(36)	122.1 (6)	C(31)-C(36)-C(35)	119.9 (5)
C(41)-N(4)-C(43)	112.0 (5)	C(41)-N(4)-C(45)	105.3 (4)
C(43)-N(4)-C(45)	111.6 (5)	C(41)-N(4)-C(47)	112.0 (5)
C(43)-N(4)-C(47)	105.5 (4)	C(45)-N(4)-C(47)	110.6 (5)
N(4)-C(41)-C(42)	115.2 (6)	N(4)-C(43)-C(44)	114.0 (5)
N(4)-C(45)-C(46)	114.3 (5)	N(4)-C(47)-C(48)	113.8 (5)
C(51)-N(5)-C(53)	112.2 (6)	C(51)-N(5)-C(55)	103.9 (5)
C(53)-N(5)-C(55)	112.6 (6)	C(51)-N(5)-C(57)	110.1 (7)
C(53)-N(5)-C(57)	106.1 (5)	C(55)-N(5)-C(57)	112.1 (6)
N(5)-C(51)-C(52)	115.3 (7)	N(5)-C(53)-C(54)	112.4 (6)
N(5)-C(55)-C(56)	114.9 (6)	N(5)-C(57)-C(58)	108.3 (6)

cascade method, to a minimum value of $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$). The weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ was used, and g was optimized automatically, the final value being 0.000 16. Scattering factors were taken from ref 9. A parameter x was refined for an isotropic extinction correction, whereby F_c becomes $F_c/(1 + xF_c/\sin(2\theta))^{1/4}$; $x = 1.4$ (3) $\times 10^{-6}$.

Final values for R ($=\sum|\Delta|/\sum|F_o|$) and for R_w [$=(\sum w\Delta^2/wF_o^2)^{1/2}$] were 0.074 and 0.093, respectively. The mean shift/esd ratio in the final cycles was 0.027; the largest values (0.1–0.2) were for rigid methyl-group rotational parameters. A final difference synthesis contained only insignificant features between 0.7 and −1.1 e Å^{-3}. The rms deviation of an observation of unit weight on an absolute scale of $|F_c|$ [$V = (\sum w\Delta^2/\sum w)^{1/2}$] was 1.93 electrons and was essentially independent of indices, sin θ, or F_o. A total of 382 parameters were refined. The rather high value of R is presumably due to the considerable thermal motion, especially of the cations.

Atomic coordinates, bond lengths, and angles are presented in Tables I and II. Parameters for hydrogen atoms and for thermal motion, together with structure factor tables, are available as supplementary material.

Results and Discussion

We have found that the reaction of $[(Ph_3PCuCl)_4]$ with $[NEt_4]SPh$ (1:20) in MeCN provides a more convenient preparative route to $[Cu(SPh)_3]^{2-}$ than that reported previously.[2]

The structure of the $[Cu(SPh)_3]^{2-}$ anion in the $[NEt_4]^+$ salt (Figure 1) resembles that in the $[PPh_4]^+$ salt, and a comparison of the salient dimensions of the anion in the two salts is presented in Table III. The major observation is that the $[Cu(SPh)_3]^{2-}$ ion more closely approximates to trigonal symmetry in the $[NEt_4]^+$ than in the $[PPh_4]^+$ salt. In particular, each of the S–Cu–S interbond angles is close to 120° in the former whereas they are markedly displaced from this value in the latter. Also, the length of the Cu–S bonds in the $[NEt_4]^+$ salt are consistently slightly shorter than those in the

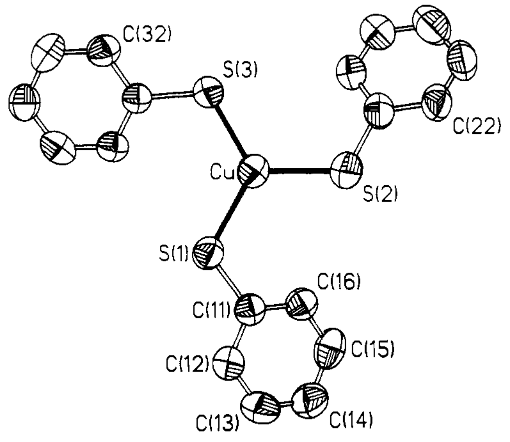

Figure 1. Structure of the $[Cu(SPh)_3]^{2-}$ ion in the $[NEt_4]^+$ salt. Thermal motion is depicted as 50% probability ellipsoids.

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(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 99, 149.

Table III. Comparison of the Dimensions of $[Cu(SPh)_3]^{2-}$ in $[NEt_4]^+$ and $[PPh_4]^+$ Salts

	$[NEt_4]_2[Cu(SPh)_3]$[a]	$[PPh_4]_2[Cu(SPh)_3]$[b]
Cu-S range, Å	2.239 (2)-2.258 (2)	2.274 (4)-2.335 (4)
Cu-S mean (esd), Å	2.250 (9)	2.295 (35)
S-Cu-S range, deg	118.2 (1)-121.3 (1)	111.7 (2)-135.4 (2)
S-Cu-S mean (esd), deg	119.9 (1.3)	120.0 (13.3)
displacement of Cu from S_3 plane, Å	0.05	0.05
S-C range, Å	1.750 (6)-1.763 (6)	1.740 (13)-1.766 (14)
S-C mean (esd), Å	1.758 (6)	1.749 (14)
Cu-S-C range, deg	113.7 (2)-115.1 (2)	107.8 (4)-114.4 (4)
Cu-S-C mean (esd), deg	114.5 (6)	110.8 (3.3)

[a] This work. [b] Reference 2.

$[PPh_4]^+$ salt. In comparison with other discrete complexes containing copper(I) coordinated to three S-donor ligands, $[NEt_4]_2[Cu(SPh)_3]$ resembles $[Cu(SPMe_3)_3][ClO_4]$[10] and $[Cu(ethylenethiourea)_3]_2[SO_4]$[11] (Cu–S = 2.253–2.264 and 2.27–2.28 Å, S–Cu–S = 118.2–122.6 and 119.7 ± 0.1°, respectively); $[Cu(tetramethylthiourea)_3][BF_4]$[11] possesses a less regular CuS_3 core (Cu–S = 2.244 ± 0.013 Å, S–Cu–S = 120.0 ± 10.9°); however, this is not as distorted as that which is obtained in $[PPh_4]_2[Cu(SPh)_3]$.[2]

The dimensions of the benzenethiolato groups of $[NEt_4]_2[Cu(SPh)_3]$ appear to be normal. The aromatic rings are all planar (rms ring (1) 0.004, (2) 0.012, (3) 0.005 Å), and these planes subtend angles of 32, 24, and 24°, respectively, with the S_3 plane. Thus, the orientations of the ligands are also much more regular and symmetrical in this structure than in the $[PPh_4]^+$ salt. The carbon atoms bonded to sulfur are each (C(11), 0.628 (5) Å; C(21), 0.502 (6) Å; C(31), −0.180 (5) Å) significantly displaced from the S_3 plane. The dimensions of the $[NEt_4]^+$ ions are unexceptional.

On the basis of comparisons of the vibrational spectra of $[NEt_4]_2[Cu(SPh)_3]$ with those of $[NEt_4]Cl$ and K[SPh], the Cu–S stretching frequencies of $[Cu(SPh)_3]^{2-}$ are considered to be responsible for the features in the vibrational spectra of $[NEt_4]_2[Cu(SPh)_3]$ at ca. 342 (Raman and IR) and 314 cm^{-1} (Raman). In D_{3h} symmetry, the Cu–S stretching modes of $[Cu(SPh)_3]^{2-}$ group as a'_1 (Raman) and e′ (IR and Raman), and thus this symmetry is consistent with the vibrational data recorded for the $[NEt_4]^+$ salt. These frequencies are in the range reported previously for metal–sulfur stretching frequencies of related complexes.[12]

The UV/visible absorption spectrum of $[NEt_4]_2[Cu(SPh)_3]$, dissolved in MeCN at ambient temperatures, consists of a distinct feature (λ_{max} = 288 nm, $\epsilon = 32 \times 10^3$ mol L^{-1} cm^{-1}) and a broad (255 > λ > 210 nm) structured band of a similar intensity. Both of these transitions are suggested to involve a considerable amount of ligand $\pi \rightarrow \pi^*$ character, since K[SPh] in MeCN has a similar UV spectral profile with λ_{max} at 298 and 250 nm.

Table IV. ^1H NMR Spectrum of the Benzenethiolato Groups of $[NEt_4]_2[Cu(SPh)_3]$[a]

chem shift[b]/ ppm	rel intens	multiplicity	J/Hz	assignt
7.33	2.1	1:1 doublet	7.5	ortho
6.79	2.1	1:2:1 triplet	7.5	meta
6.61	1.0	1:2:1 triplet	5.5	para

[a] Recorded in CD_3CN at 24 °C. [b] δ scale, referenced to Me_6Si_2 at 0 ppm.

Solutions of $[NEt_4]_2[Cu(SPh)_3]$ are extremely sensitive to reaction with air, whence a green coloration rapidly develops; a similar reaction occurs in the solid state. $[PPh_4]_2[Cu(SPh)_3]$ is orange in *both* the solid state[2] and solution. The UV/visible spectrum of this latter salt in $MeCN/Et_2O$ solution shows that the origin of this color is the displacement of the absorption at 288 nm of $[NEt_4]_2[Cu(SPh)_3]$ to ca. 320 nm. This red-shift is presumably a consequence of the interactions between the $[PPh_4]^+$ and $[Cu(SPh)_3]^{2-}$ ions, which significantly alter the properties of the latter as compared to those observed in the $[NEt_4]^+$ salt. Thus, the interionic associations predispose the anion to dissociation into $[Cu(SPh)_2]^-$ and $[SPh]^-$ ions, as manifest in the crystal structure of $[PPh_4]_2[Cu(SPh)_3]$ and in the isolation of $[PPh_4][Cu(SPh)_2]$ upon recrystallization of $[PPh_4]_2[Cu(SPh)_3]$, unless carried out in the presence of an excess of $[SPh]^-$.[2] In contrast, the successful recrystallization of $[NEt_4]_2[Cu(SPh)_3]$ does *not* require added $[SPh]^-$. Some evidence of significant interaction between the phenyl rings of the anion and the cations in $[PPh_4]_2[Cu(SPh)_3]$ has been found in short interionic contacts in the crystal structure. Although crystal-packing forces are obvious candidate for the cause of the difference in the geometry of the anion in the two salts, the interionic interactions must persist in solution. In any case, it is reasonable to regard the more symmetrical form of the anion in the $[NEt_4]^+$ salt as "normal" and that in the $[PPh_4]^+$ salt as perturbed.

The details of the ^1H NMR spectrum of the anion of $[NEt_4]_2[Cu(SPh)_3]$ (Table IV) are as expected and are consistent with the anion dissolving as a simple, single species. Each of these resonances are displaced upfield of the corresponding value[13] for K[SPh] (in $(CD_3)_2SO$ solution) by 0.14–0.40 ppm, and the coupling constant for the para proton is reduced by ca. 2 Hz.

Acknowledgment. We thank the SERC for the provision of a studentship (to J.R.N.), the Verband der Chemischen Industrie for financial support (to W.C.), and A. H. Palmer for technical assistance.

Registry No. $[NEt_4]_2[Cu(SPh)_3]$, 90029-98-4; $[(Ph_3PCuCl)_4]$, 50409-58-0.

Supplementary Material Available: Listings of calculated atomic coordinates, anisotropic thermal parameters, isotropic thermal parameters, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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